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Miniature time-of-flight mass spectrometer using a flexible circuitboard reflector

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An innovative design for a miniature time-of-flight mass spectrometer has been developed employing several newly designed components. These include: (1) a gridless, focusing ion source allowing for the use of very high extraction energies in a maintenance-free design, (2) a new method of construction for an ion reflector using rolled flexible circuitboard material, and (3) an improved center-hole microchannel plate detector assembly that significantly reduces the noise (or 'ringing') inherent in the coaxial design. A prototype time-of-flight instrument was constructed and used to evaluate the performance of these components. Compared to previous designs, results indicate that background noise for data acquired on this instrument is substantially reduced, resolution is improved, and the potential for mass producing this instrument in an inexpensive and rugged package for field-portable and remote installations is significantly enhanced.

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Miniature time-of-flight mass spectrometers (TOF-MS) have the potential to be used in numerous field-portable and remote sampling applications due to their inherent simplicity and potential for ruggedization.[1,2] Conventional wisdom, however, holds that a compact TOF-MS would not have sufficient drift length to achieve high performance, as measured by good resolving power or the capability to detect and identify product ions. These capabilities, currently found only in laboratory grade instruments, would greatly enhance the utility of a field portable TOF-MS. Without the benefit of an extended drift region (and thereby long flight times), good resolution can only be achieved in a compact TOF-MS if the ion peaks are quite narrow. All aspects of the miniature analyzer and ionization processes that affect ion peak widths must therefore be optimized for minimum peak broadening. Commercially available short-pulse lasers and fast transient digitizers enable the creation and measurement of very narrow ion signals, but the ion source region, reflector performance, and detector response will each contribute to the final peak width as well. To this end, new components have been developed for the miniature TOF-MS that improve its overall performance. Three advances are described here: (1) a focusing ion extraction source, (2) a miniature flexible circuitboard reflectron, and (3) a low-noise channelplate detector assembly. These have been developed with special additional attention paid to ruggedness and durability for operation under remote and harsh environmental conditions.

INSTRUMENTATION

Focusing ionization source

To increase the collection efficiency of laser-desorbed ions from a surface, a gridless focusing ionization source has been designed. Using a series of closely spaced cylinders (Fig. 1), an extremely high extraction field is created (up to 10 kV/mm) between the flat sample probe (at +5 kV) and an extraction cylinder (at −5 kV). Once accelerated, the ions are slowed immediately in a retarding field, serving both to collimate the ion beam as well as to reduce the ion velocity. Figure 1 also displays a 3-D SIMION[3] diagram of the ionization source showing the potential gradients formed by the applied voltages of each electrostatic element. This combination of lens elements minimizes losses caused by radial dispersion of ions generated in the desorption plume. Although this source design employs a very high extraction field, the ions are slowed prior to entering the drift region resulting in longer drift times and hence increased ion dispersion. Furthermore, the performance of the source is achieved without the use of any grids, thus eliminating transmission losses, signal losses due to field inhomogeneities caused by the grid wires, as well as the need for periodic grid maintenance.

Flexible circuitboard reflector

Ion reflectors have become a standard part in many time-of-flight mass spectrometers since their development 30 years ago.[4,5] While there have been improvements in reflector performance by modifications to the voltage gradients,[6–8] the mechanical fabrication is still based on stacked rings in most laboratory instruments. In this design, metallic rings are stacked along ceramic rods with insulating spacers separating each ring from the next. While this has been proven to be satisfactory for the construction of large reflectors, new applications of remote TOF mass analyzers require miniaturized components, highly rugged construction, lightweight materials, and the potential for mass production. To this end, a new type of ion reflector has been developed utilizing the precision of printed circuitboard technology and the physical versatility of thin, flexible substrates. A series of thin copper traces (0.203 mm wide by 0.025 mm thick) are etched onto a flat, flexible circuitboard substrate such as Kapton (Fig. 2). The circuitboard is then

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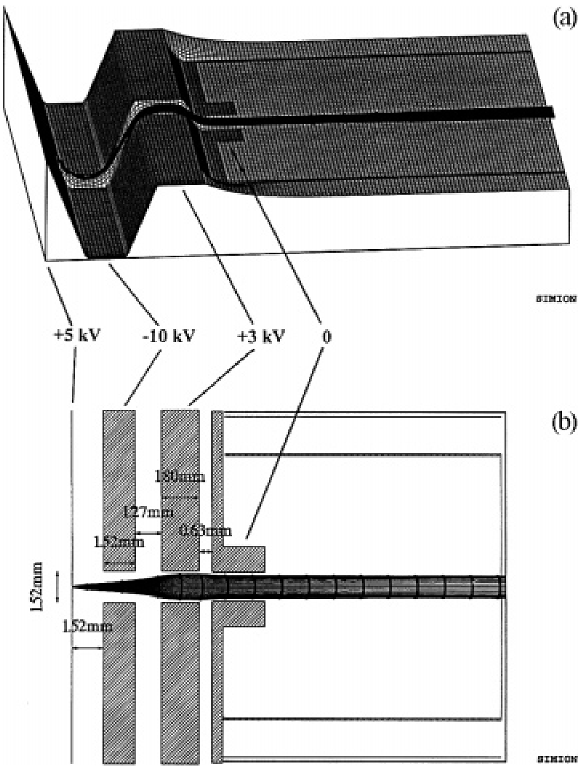

Figure 1. (a) SIMION 3-D potential energy representation of the gridless focusing ionization source. (b) Cross section of the ion source showing physical dimensions.

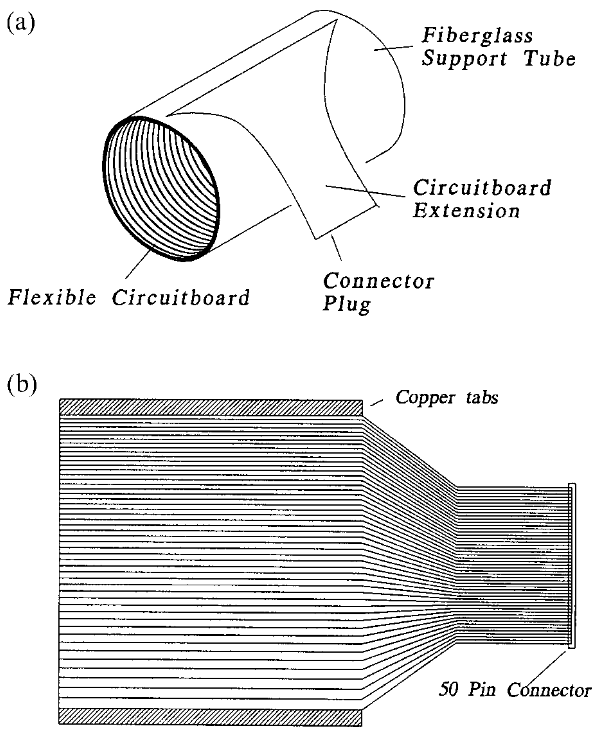

Figure 2. (a) Diagram of a completed reflector. The flexible circuitboard is rolled and encased within a fiberglass shell. (b) Flexible circuitboard sheet with copper traces etched onto the surface. A ribbon connector is attached to the tapered end for connection to a voltage divider network.

rolled into a tube to form the reflector body, with the copper traces facing inward, forming the isolated rings that define the voltage gradient. The thickness and spacing of the traces can be modified by simply changing the conductor pattern on the substrate sheet during the etching process. This feature is particularly useful for the production of precisely tuned non-linear voltage gradients, which are essential to parabolic or curved-field reflectors.[6–8] The trace pattern on the circuitboard diagram shown in Fig. 2 represents a precision gradient in the spacing of the traces. Thus, in the resultant reflector, a curved potential gradient is generated by employing resistors of equal value for the voltage divider network. For data reported in this study, the reflector was constructed from a circuitboard with equally spaced traces used in conjunction with a series of potentiometers to establish a curved potential gradient similar to a design reported earlier.[8] Product ions, if present in the data, should therefore be observed.

Once etched, the circuitboard substrate is rolled around a mandrel to form a tubular shape as shown in Fig. 2(a). Five layers of fiberglass sheets, each approximately 0.25 mm thick, are then wrapped around the circuitboard substrate. The length of the curving edge of the board is approximately equal to the circumference of the mandrel. When the sheets are wrapped around the rolled circuitboard, a slight opening remains through which the connector end of the inner circuitboard can extend. The position of each successive sheet is offset slightly with respect to the previous sheet so that a gradual 'ramp' is formed, thereby guiding the flexible substrate away from the mandrel.

The reflector assembly is heated under pressure at 150 °C for approximately 2 h, followed by removal of the mandrel. Wall thickness of the finished rolled reflector assembly is approximately 1.5 mm. A 50-pin ribbon-cable connector is soldered onto the protruding circuitboard tab so that a voltage divider resistor network can be attached to the reflectron. Alternately, soldering pads for surface-mount resistors can be designed into the circuitboard layout, allowing the incorporation of the voltage divider network directly onto the reflector assembly. Finally, polycarbonate end cap plugs are fitted into the ends of the rolled reflectron tube to support the assembly as well as provide a surface for affixing terminal grids. Vacuum tests indicate that this circuitboard and fiberglass assembly is capable of achieving vacuum levels in the low 10^{-7} Torr range.

Pin anode detector

For miniature TOF mass spectrometers, the center-hole (coaxial) geometry is a highly desirable configuration because it enables the simplification of the overall design and allows for the most compact analyzer. However, the poor signal output characteristics of center-hole microchannel plate detector assemblies, particularly the problem with signal 'ringing', clutter the baseline and, as a consequence, adversely affect the dynamic range of the instrument. This limitation severely reduces the chance of realizing high performance in miniature TOF instruments since low intensity fragment or product ion peaks can be obscured by baseline noise. Improvements to the analog signal quality of center-hole channelplate detectors would therefore increase the ultimate performance of the mass spectrometer, particularly the dynamic range.

Commercially available coaxial channelplate detectors rely upon a disk-shaped center-hole anode to collect the

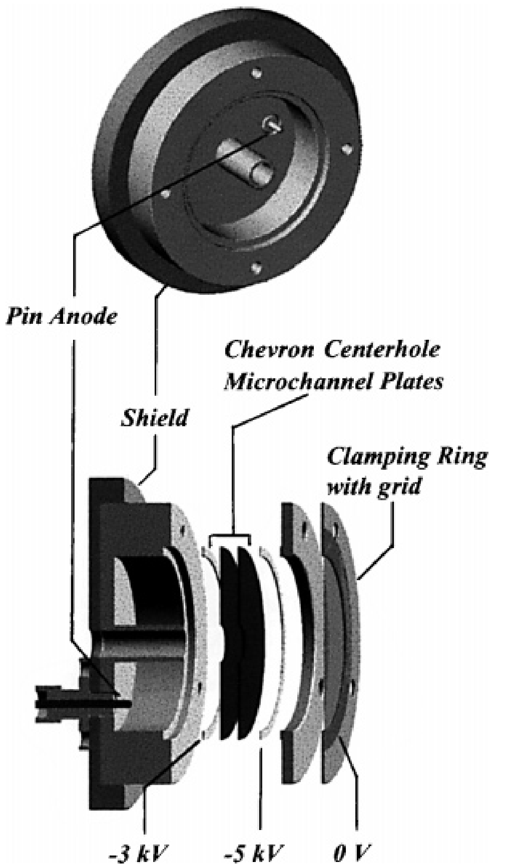

Figure 3. CADD drawing of the pin anode coaxial channelplate detector enclosure and cutaway view showing the internal components.

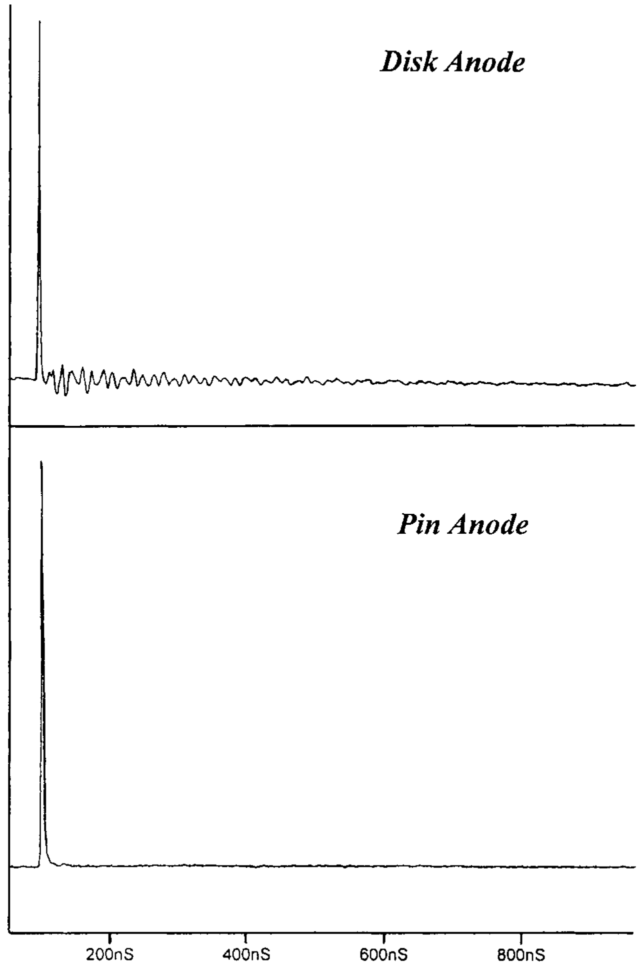

Figure 4. Comparison of the single ion signal from a conventional vs. pin anode detector. Each trace represents the averaged spectrum of several hundred pulses.

pulse of electrons generated by the microchannel plates. The anode is normally matched to the diameter of the channelplates, thereby, in theory, maximizing the electron collection efficiency. However, the center-hole anode creates an extraneous capacitance within the grounded mounting enclosure. The center-hole anode also produces a significant impedance mismatch when connected to a 50Ω signal cable. The resultant ringing degrades and complicates the time-of-flight spectrum by adding a high frequency component to the baseline signal. Moreover, the disk-shaped anode acts as an antenna for collecting stray high frequencies from the surrounding environment, such as those generated by turbo-molecular pump controllers. A simple, physical alteration of the collection anode (discussed below) has been found to substantially improve the overall performance of the detector.

For enhanced sensitivity, the entrance grid of the detector assembly (Fig. 3) is held at ground potential while the front surface of the channelplate is set to −5kV, post-accelerating ions to 5 keV. Using voltage divider resistors, the rear of the channelplate assembly is held at −3kV. Since the collection anode is isolated from the detector assembly, its potential is defined by the oscilloscope's front end amplifier (nominally ground). Thus, electrons emitted from the rear channelplate will be accelerated toward the grounded anode regardless of the anode's size, geometry, or location. It is found that a small, polished pin anode located about 5 mm behind the rear channelplate significantly improves the overall performance of the detector. This design virtually eliminates the impedance mismatch between the 50Ω signal cable and the electron collection surface (the pin). Figure 4 compares the single ion detector response for both the center-hole and the p/n anode configurations. Ringing is significantly reduced and the ion pulse width (FWHM) is reduced to a value of 500 ps/pulse, limited by the analog bandwidth of the oscilloscope used for the measurement (LeCroy LC-684 DXL: 1.5 GHz: 8 Gsamples/s). Furthermore, the background signal in the time-of-flight data caused by spurious noise is found to be much quieter when the pin anode is installed.

RESULTS

Figure 5 depicts the prototype TOF-MS incorporating the focusing ion source, the flexible circuitboard reflector, and the micro-anode channelplate detector. The overall length of the entire analyzer is approximately 25 cm. A nitrogen laser (LSI VSL-337I) was used for acquiring MALDI and laser ablation spectra. Time-of-flight data were acquired on a LeCroy 9384 digital oscilloscope (1 GHz: 2 Gsam/s) used in conjunction with Tofware spectrum acquisition software (Ilys Software).

Several different types of samples were used to test the performance of the analyzer. Surface roughness was an important consideration because heavily pitted surfaces or organic samples with enlarged crystal formation can significantly increase the distribution of ion kinetic energies in the very high field extraction region. Samples were

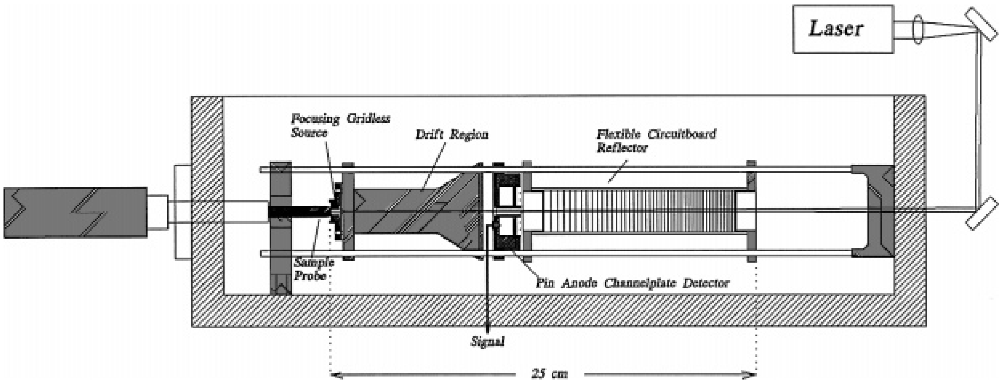

Figure 5. Diagram of the complete time-of-flight mass analyzer using the gridless ionization source, flexible circuitboard reflector, and the pin anode channelplate detector. The laser beam enters the vacuum chamber from the end opposite the source region and is focused along the flight path of the ions.

therefore prepared to ensure a smooth desorption surface. Figure 6 displays the direct laser desorption signal obtained from a clean Pb solder surface in which spectra from 20 consecutive laser shots were acquired and averaged. Isotopic distributions from both the major Pb and minor Sn components are clearly resolved. Peak widths at half-maximum are approximately equal to the 5 ns laser pulse width (resolution m/Δm *approx* 1000).

Also shown in Fig. 6 is the averaged MALDI spectrum (25 laser shots) of angiotensin II using α-cyano-4-hydroxycinnamic acid as the matrix. Isotopic separation of the MH^{+} peak at 1047 Da represents a resolution of greater than 1500. Additionally, between 600–1000 Da, there is a series of peaks formed by post source decay (PSD)[9] of the precursor peptide indicating that the curved-field reflector is focusing product ions as anticipated. Further refinement and optimization of the reflector's wide energy range focusing capabilities are required to increase the sensitivity for PSD ions, an effort currently in progress.

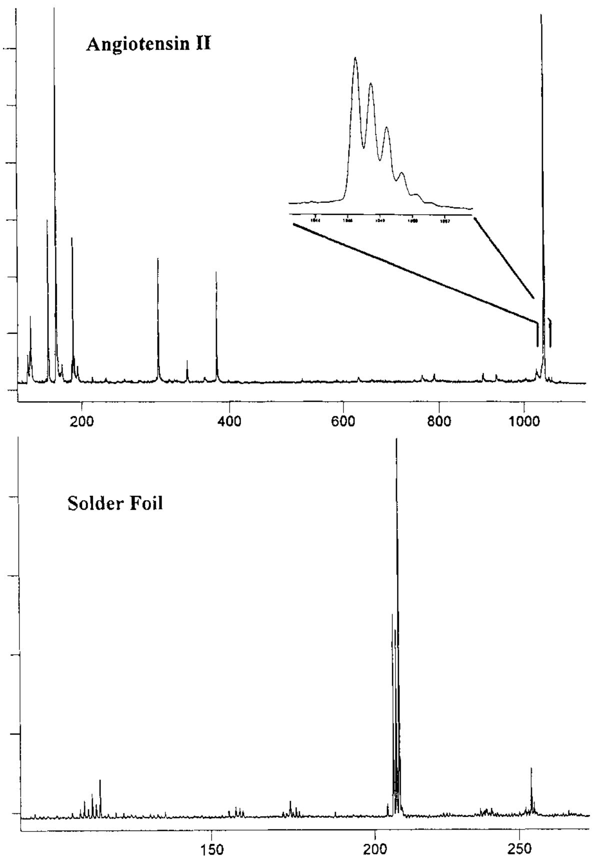

Figure 6. Spectra of angiotensin II and solder foil collected on the miniature TOF mass analyzer.

CONCLUSIONS

An innovative, compact time-of-flight mass spectrometer has been developed using a gridless focusing source, flexible circuitboard ion reflector, and pin anode channelplate detector. Preliminary evaluation of the new instrument indicates it is capable of producing spectra with very good resolution and low background noise, a problematic feature of many coaxial TOF instruments. The analyzer can also be made quite rugged, and is readily adaptable to mass production.

Several remote sampling projects utilizing this new design are currently underway, including field-portable biological and chemical weapons detection[10] and *in situ* analysis of geological samples on planetary bodies.[11] A further potential use of the miniaturized TOF-MS is to array or 'bundle' multiple analyzers within a single instrument for extremely rapid parallel data collection. In this configuration, the throughput of 'chip reading' time-of-flight mass spectrometers used in proteomics and genomics applications may be increased manyfold.

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